Novel Processing of a Poly(phenyleneoxide) –*b*–Poly(vinylbenzyltrimethylammonium) Copolymer Anion Exchange Membrane; The Effect On Mechanical And Transport Properties

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Graphical_abstract

Abstract

A poly(2,6 dimethyl 1,4-phenylene oxide)-*b*-poly(vinyl benzyl) chloride copolymer membranes was processed by solvent casting followed by melt pressing (SCMP) to provide uniformly thin films, $25 \pm 5 \mu\text{m}$, with improved conductivity, mechanical strength, water uptake, dimensional swelling, and chemical stability under 1 M KOH and 80 °C. These properties depended strongly on the length of the melt-pressing time. The solvent cast membranes melt pressing time was optimized to provided highly conductive membranes (high OH⁻ conductivity of $75 \pm 25 \text{ mS}\cdot\text{cm}^{-1}$ for an IEC of $1.8 \text{ mmol}\cdot\text{g}^{-1}$ at room temperature in water). Membranes that were only solvent cast and not melt-pressed swelled excessively and had insufficient mechanical

integrity for detailed study. When the copolymer powder was melt pressed (without prior solvent casting) at 240 °C and *ca.*30 MPa for 20 minutes, membranes with high mechanical strength (tensile stress at break of 32 ± 6 MPa at 25%RH and 29 ± 3 MPa when 95%RH at 60 °C), high conductivity (Cl^- conductivity of 80 mS/cm at 90 °C and 95%RH), and lower water uptake were formed. However, melt pressing alone did not give larger than 5 cm $\times$ 5 cm area films, homogeneously thin (< 60 μm), or mechanical defect-free membranes. The SCMP membranes were uniformly thin, and thermally crosslinked. The mass loss *via* dehydrochlorination indicated by TGA and elemental analysis confirmed the crosslinking *via* thermal melt pressing. The SCMP membranes thickness could be reduced by more than 50% ($25 \pm 5\mu\text{m}$) compared to melt pressing alone, and the Cl^- conductivity increased by 44% at 90 °C and 95%RH. The tensile stress at break of the SCMP membranes, however, was reduced by 50% at 25%RH.

Keywords: Fuel cells, Anion exchange membranes, alkaline conductivity, poly(2,6 dimethyl 1,4-phenylene oxide), benzyl trimethyl ammonium cations

1 Introduction

Anion exchange membrane (AEM) fuel cells and other electrochemical energy conversion devices are currently being intensively investigated as they may have several advantages over proton exchange membrane (PEM) fuel cells and related devices will facilitate complimentary electrocatalysis in basic media [1]. The PEM fuel cells require precious metal catalysts, such as, platinum, to catalyze the hydrogen oxidation and oxygen reduction reactions and the oxidation of many fuels beyond hydrogen is challenging in acid media. Perfluorosulfonic acid membranes, such as Nafion[®] [2], do not solve the water management issues of PEM fuel cells, utilize fluorine chemistry that could be environmentally challenging, and when thin allow

too much hydrogen cross-over. AEM fuel cells with non-platinum catalysts, such as nickel and cobalt have already shown promising fuel cell performances [3-6]. However, a practical AEM for a fuel cell, will need to simultaneously to have high anionic conductivity over a wide range of humidity and temperatures up to and above 80 °C, excellent water transport properties, prevent fuel and oxygen crossover, maintain chemical stability, and exhibit mechanical durability over the lifetime of the device and be amenable to large surface area manufacturing.

Transport of OH^- in AEMs was thought to be slower than H^+ in PEMs due to the larger ionic size of the OH^- , however several examples of materials with high hydroxide conductivity are now known [7, 8]. Increased OH^- transport by increasing the ion exchange capacity (IEC) of a membrane has been demonstrated; Ran *et al* have shown that the increase in IEC leads to larger water uptake that enhances ion transport giving a higher ionic conductivity [9]. However, the larger water uptake and dimensional swelling can compromise the mechanical strength of polymer membranes [10]. Increasing IEC does not guarantee higher conductivity, and Ertem *et al.* have observed that the ionic conductivity increases with increasing IEC up to 1.54 mmol.g^{-1} and then is level at higher IECs for random copolymers of poly(isoprene) and poly(vinylbenzyl chlorine) AEMs [11]. With sufficient water uptake, the water in the membranes reaches a dilution limit (i.e., approximates an aqueous solution), exhibiting the water diffusion values that approach bulk water diffusion. The diffusion is directly related to the ionic conductivity and the conductivity is limited by the maximum diffusion of ions at the limiting IEC of AEMs. Hence, optimization of the IEC to maximize mechanical, transport and chemical properties is crucial.

Different polymers with various contents of ionic groups [12], cross-linking [12-14], and different combinations of backbones and cations have been considered for improving AEM performance [1]. Hydrophobic polymer backbones can provide mechanical strength, while the

cation provides the ionic transport properties for good performance. The use of aliphatic hydrocarbons for polymer backbones gives a flexible, elastic backbone while aromatic backbones create stiffer membranes [15]. The literature has indicated the degradation of polymer backbones and cations at alkaline environments [16]. Chemical stability of an alkaline AEM is one of the most pressing challenges in AEM fuel cells. The OH^- is highly nucleophile that attacks AEM cations or backbones and leads to chemical degradation. More complex and larger cations, such as phosphonium, sulfonium, cationic ruthenium complexes, and cobaltocenium groups, for cation/chemical stability at high temperatures have been explored [17-20]. Gu *et al* have explored a range of these cations including larger cations, such as, cobaltocenium, phosphonium, and sulfonium for cation lifetime durability [17-19], and recently Marino and Kreuer, have shown that simple nitrogen hetrocyclic cations may have enhanced stability [21].

Smaller cationic head groups such as those formed by quaternization with trimethlyamine (TMA), especially benzyltrimethyl amine (BTMA) are easy to tether to the polymer backbone and are stable at low temperatures [21, 22]. Quaternary ammonium cations have actually shown great chemical stability and high ionic conductivity in alkaline environments when operated at 80 °C in some cases [1, 7, 12, 21, 23, 24]. Deavin *et al.* and several other groups have used different experimental techniques to show very little to no degradation of benzyl trimethyl ammonium groups in their systems when operated at 60-80 °C and alkaline environments [22, 25, 26].

High ionic conductivity is important to get good performance in a fuel cell but for high power density in fuel cells, we need thinner membranes to give low area specific resistance (ASR). So the mechanical integrity of the membrane is crucial as we seek to make thinner materials, especially over the lifetime of the device. As water is needed to obtain high ion

transport, and the membrane needs to transport water back from the anode where it is produced to the cathode where it is consumed and the effect of water on the mechanical properties should be understood and controlled. Controlling water uptake prevents membrane swelling and ultimately preserves mechanical integrity. Different approaches have been explored to enhance mechanical stability of AEMs without losing chemical or transport properties. Introduction of more hydrophobic polymer backbones, aromatic backbones [27-29], introduction of cross-linking, lower IECs, and thermal treatment, etc., are a few ways to make mechanically strong AEMs. Robertson *et al* have shown that cross-linking hydrophilic groups can increase ionic conductivity and mechanical strength of polymer membranes [14].

In previous work [8, 12] solvent cast Polyphenyleneoxide –b–Polyvinylbenzyl (PPO-*b*-PVB) chloride membranes were prepared using a 12 wt.% copolymer-chloroform solution to provide a transparent, uniformly thick, and defect-free membrane before the quaternization reaction. When the membranes were soaked in an aqueous liquid TMA solution for the quaternization reaction to give Polyphenyleneoxide –b–Polyvinylbenzyltrimethylammonium (PPO-*b*-PVBTMA) copolymer films, the membranes swelled significantly. Excessive swelling in liquid water was also observed after quaternization from the vapor from a TMA solution and the membranes formed were too brittle to handle. Hence, an in-depth study of the solvent cast membranes was not pursued further. The literature has reported an increase in membrane strength by increasing cross-linking [10, 11, 30, 31]. Alternatively, melt pressing of the copolymer at 240 °C and 30 MPa created an insoluble membrane with controlled swelling, reduced water uptake, and greater mechanical strength. Melt pressing of copolymers with different IECs provided mechanically strong and highly conductive membranes as described in earlier publications [8, 12]. However, the melt pressing provided non-uniform (50 – 115 μm)

membranes had some mechanical defects, such as pinholes, due to the difficulty in controlling the flatness of surface and temperature gradient over a large sample area. The production of larger surface area membranes for device level studies, such as a membrane for fuel cell testing, was limited by the large variation in thickness, possible presence of pinholes, and difficulty in replicating membrane thickness between batches.

In this paper we present a study of the processing parameters for a set of promising PPO-*b*-PVBTMA diblock copolymers [8, 12] with benzyl trimethyl ammonium cations, with the goal of making thinner higher performing membranes. To achieve this the precursor PPO-*b*-PVB chloride polymers were solvent cast and then melt pressed for various times to prepare materials with various levels of cross-linking. The films were then assessed in terms of their chemistry, swelling, chemical stability, and ionic conductivity.

2 Experimental

2.1 Materials and membrane processing

The poly(2,6-dimethyl 1, 4 phenylene oxide) – *b* – poly(vinyl benzyl chloride) (PPO-*b*-PVB chloride) block copolymer was synthesized using a previously published procedure [12]. The starting compositions of PPO and PVBC were *ca.* 30 and 70%; respectively and molecular weight of 85 kg/mol measured using gel permeation chromatography [12].

The diblock copolymer powder was vacuumed dried for 24 h at room temperature and used as a starting material for making AEMs. A 12 wt.% solution of PPO-*b*-PVB chloride was prepared in chloroform. A vortex mixer (VWR Analog Vortex Mixer) was used to dissolve of the copolymer powder completely and form a homogenous solution. The solution was dropped on a Teflon sheet and created thin membranes by drawing a Doctor Blade with blade gap of 200 μm . The cast membrane was dried first at ambient conditions for 24 h and then under vacuum for 24 h before the membrane was peeled off and used as a starting material for solvent cast and melt

press processing. The solvent cast only membranes (SC) were quaternized with vapor 25 wt. % TMA solutions to give PPO-*b*-PVBTMA materials for water uptake study.

For melt pressed only membranes (MP), the dried powder was spread out evenly between two flat blocks of Teflon and pressed between two heating plates (Carver® Model 3912 press) at 240 °C and *ca.*30 MP for 20 min. For SCMP processed membranes, the solvent cast membranes before the quaternization reaction were placed between Teflon sheets and pressed by the two stainless steel platens of the press with 30 MPa at 240 °C as a function of pressing time. Solvent cast membranes melt pressed for 5, 10, or 20 min were abbreviated as SCMP5, SCMP10, and SCMP20 respectively. After melt pressing, all membranes, MP, SCMP5, SCMP10, and SCMP20, were reacted with trimethyl ammine (Fisher Chemical) TMA by soaking in 45 wt.% TMA solutions for 24 h to give PPO-*b*-PVBTMA. The quaternized membranes were washed with deionized water before further studied.

2.2 Ion exchange capacity (IEC)

The IEC of the membranes was determined by titration of chloride ions in solutions using Mohr's titration method. The chloride form of the membrane was soaked in 1M NaNO₃ for 48 h, and aliquot of the solution was then titrated with standardized 0.0510 M silver nitrate solutions. Dilute 5% potassium chromate indicator determined the end point for the titration by rust colored precipitation.

$$\text{IEC (mmol.g}^{-1}\text{)} = \text{Vol. AgNO}_3 \times \text{Conc. AgNO}_3 \times 1 \text{ mol Cl}^- / 1 \text{ mol Ag}^+ \times 1 / (\text{g dry polymer})$$

Dry mass was measured after vacuum drying the sample membranes at 30 °C for 24 h.

2.3 Elemental Analysis

To quantify the amount of chlorine, nitrogen, and oxygen in the membranes before and after processing, the element analysis was performed using modified method ASTM E442-91 in

an independent laboratory (Huffman Hazen Laboratories, Golden, CO). The precursor powder copolymers and AEMs in chlorine form for the elemental analysis were prepared by vacuum drying all samples for 24 h at room temperature. Three replications were performed on different batches of samples to average out the data.

2.4 Thermogravimetric Analysis (TGA)

The TGA was performed using TGA Q500 V20.13 (TA Instruments) on the PPO-*b*-PVB chloride to study the effect of temperature during melt pressing. The powder sample was vacuum dried for 12 h before the measurements. The sample was heated to 240 °C using the heating rate of 10 °C per minute and was hold at the temperature for 40 min under air to mimic the melt pressing environment that was used in the membrane processing.

2.5 Fourier Transform Infra-red Spectroscopy (FTIR)

The FTIR (Nicolet Nexus 4700) with an ATR (Specac Inc.) attachment was used to collect IR spectra over a range of 4000 - 600 cm⁻¹ at the 4 cm⁻¹ resolution with 256 scans. A liquid nitrogen cooled MCT detector was used to collect spectra at ambient conditions of temperature and humidity. The FTIR spectra were collected for dried precursor PPO-*b*-PVB chloride copolymer in powder form before and after melt pressing.

2.6 Vapor water uptake and dimensional swelling

A dynamic vapor sorption (DVS) instrument (Surface measurement systems DVS Advantage 1) measured water uptake by membranes. A small sample *ca.* 4 - 10 mg was vacuum dried for 12 h and then loaded in a glass plate, and the change in mass measured under different humidity conditions. The water uptake was calculated as: Membrane water uptake (WU) = $(m_{\%RH} - m_{dry}) / m_{dry} \times 100\%$. Where, $m_{\%RH}$ is the mass of the sample at the given humidity and m_{dry} is the dry mass of the sample. The dry mass of the sample was taken at the end of the 3 h drying period. Time required to attain both the long and short term steady state of water uptake

was determined for the study. With the saturated water uptake values and the ion exchange capacity of the membrane, the hydration level of the membrane, (λ), which is the number of water molecules per cation group, was calculated by: $\lambda = \text{WU} / (\text{IEC} \times \text{MW}_{\text{H}_2\text{O}} \times 100)$

2.7 *Liquid water uptake and Dimensional Swelling*

Liquid water uptake by the membranes was measured by taking the weight of the dry and wet membranes. Membranes were vacuum dried at 30 °C for 24 h for dry measurements and soaked in liquid water for 24 h at room temperature and patted dry with lint free wipes (kimwipe™) for the wet measurements. The detail procedure for the measurements and the dimensional swelling calculations are published elsewhere [8].

2.8 *Pulse field spin-echo-NMR (PFSE-NMR)*

For the measurement of the self-diffusion coefficient of water in the AEMs, solid membrane samples of about 100 mg were rolled and inserted into a NMR tube. For water saturation environments, a water reservoir was created at the bottom and another capillary tube full of liquid water was inserted above the membrane samples. The tube was capped and made airtight with a Teflon shield to prevent water escaping from the tube. The prepared samples were left at least 48 h to equilibrate with water before the NMR measurement. Measurements were performed as a function of diffusion time at constant temperature from 30 to 50 °C. The detailed procedure for the sample preparation and experimental setups are described elsewhere [7].

2.9 *In-plane ionic conductivity and area specific resistance*

In-plane ionic conductivity of the membranes in chloride and bicarbonate forms was measured using the same procedure published earlier [7]. For a membrane of width, w , thickness, t , the distance between the sense electrodes, $l = 0.425$ cm, and the membrane resistance R , and the conductivity is calculated as; $\text{conductivity} = l / (R \cdot w \cdot t)$

The OH⁻ conductivity measurements in liquid water conditions was measured for the SCMP10 samples at 20 °C by immersing the membranes in degassed DI water during the measurement of the EIS spectra. The SCMP10 membrane was ion exchanged to the OH⁻ by soaking the membrane in 1M KOH solutions for 24 h with replacing the KOH solution twice for a complete ion exchange. The membrane was then rinsed with Argon degassed DI water several times over a period of several hours.

To understand AEM stability the membranes were soaked in 1 M KOH and maintained at 80 °C in an air free environment. At various times over 12 days, samples were taken out of the KOH solution, converted to the HCO₃⁻ form by soaking in 1 M NaHCO₃ solution for 24 h followed by washing with DI water for 12 h, and then the HCO₃⁻ conductivity was measured at 80 °C and 95%RH.

2.10 Mechanical characterization from tensile testing

Mechanical properties of the membranes were measured using an ARES G2 rheometer (TA instruments) with a SER universal testing fixture (Xpansion Instruments). Membrane samples, about 3 mm wide and 20 mm long, were loaded between two counter rotating drums with clamps [32] and stretched until the stress at failure with a fixed strain rate of 0.01 s⁻¹. The temperature and humidity of the samples were controlled using a custom built oven [32]. The humidified gas flow controlled by mass flow controllers, was used to maintain the dry and wet environment of the samples. The membrane hydration level was measured using a humidity probe (Vaisala HMT337). Samples were equilibrated for 10 min for the dry and 60 min for the wet measurements. Using the stress-strain response, Young's modulus, stress at break (ultimate strength), and percent elongation were calculated [33].

2.11 Small angle x-ray scattering (SAXS)

Small angle x-ray scattering experiments were performed at the Advanced Photon Source, Argonne National Laboratory (IL, USA), beamline 12-ID-B with a transmission mode using a Pilatus 2M SAXS detector. Incoming x-ray beam energy of 12 keV with an exposure time of 1 s was used for all samples. Radially integrated 2D scattering intensity was measured over a range of scattering vectors (q). Temperature and humidity of the samples were controlled using a custom-built oven with four sample holders. The ratio of dry and wet compressed N₂ gas flowing through the oven regulated humidity and temperature. Temperature, humidity, and equilibration time were matched with the conditions for the water uptake study using the DVS instrument. A detailed experimental set up for the temperature and humidity control systems is published elsewhere [34]. A Kapton[®] tape background pattern (without any sample) was collected for all experimental conditions and used as background.

3 Results/Discussion

3.1 Membrane processing

Membranes were first solvent cast from chloroform, and then melt pressed as a function of time. The solvent cast films were 20 – 30 μm uniformly thick membranes, with surface areas $>25\text{ cm}^2$, that gave transparent brown films on quaternization. The melt pressing was presumed to introduce thermal cross-linking improving mechanical strength and dimensional swelling. To understand the chemical compositions of the membranes after processing, analytical analysis was performed on both precursor and post processing samples.

The membranes were melt pressed at 240 °C as this was determined to be above the $T_{g,s}$ by DSC but below the on-set of degradation in a 10 °C/min TGA scan in N₂ [12]. However, it was inferred that some cross-linking must occur at 240 °C and so to determine the length of time to melt press the membranes we examined the mass loss at 240 °C in air, by TGA, Figure 1. The

total mass loss, was observed to be 6 wt.% over just more than 20 minutes and so we chose to melt-press the film for 5, 10 and 20 minutes to obtain films with variable amounts of cross-linking.

3.2 Membrane Characterization

Elemental analysis gave the %w/w of chlorine, nitrogen, and oxygen in the samples. The concentration of the chlorine %w/w in the polymer membrane after processing decreased from the initial concentration in the precursor samples. The initial precursor copolymer powder showed the presence of 14.3 %w/w of chlorine that decreased with melt pressing (Table S1). The chlorine concentration decreased dramatically, 41-44% with melt pressing at 5 min but then leveled off at around the same values with longer melt pressing times, in contrast to the open pan unrestrained TGA, Figure 1. Oxygen element analysis performed on a different batch of the copolymer indicated no change in concentration of oxygen during processing, which confirms the stability of the PPO backbone and that the mass is lost from the PVBC block of the copolymer. The nitrogen element analysis performed on quaternized AEMs Table S1 indicated that the nitrogen content remains nearly constant with melt pressing time, indicating no further loss of chlorine in the polymer with longer melt pressing times. This indicates that cross-linking maybe complete after 5 minutes and that the longer melt-pressing times are melting and organizing the residual PVBC block of the polymer. However, as will be shown below the samples melt-pressed for longer behave though they have higher levels of cross-linking, lower IEC, less swelling in water *etc.*

To determine the nature of the cross-links, qualitative analysis of the precursor copolymer PPO-*b*-PVB chloride and the resultant diblock PPO-*b*-PVB-TMA membranes was performed using ATR-FTIR (Figure S1). The existence of medium intensity $\nu(\text{=C-H})$ at *ca.* 3024 cm^{-1} , $\nu(\text{-C=C-})$

at *ca.* 1644 cm⁻¹, and $\delta(-C=C)$ at *ca.* 890 cm⁻¹ indicated the presence of aliphatic C=C bonds after melt-pressing. This suggested that elimination of chlorine and carbon-carbon double formations was the cross-linking mechanism. However, a Friedel-Crafts mechanism of the vinyl benzyl chloride group has also been reported and can not be ruled out [35, 36]. The $\nu(C-O)$ at *ca.* 1180 cm⁻¹ from the PPO block remains the same before and after melt pressing, again indicating that the PPO block was unaffected during the melt pressing process.

Using the wt.% of chlorine in the membrane from the elemental analysis, the ion exchange capacity (IEC) was calculated using the following relation to compare with the titrated IEC of the membranes, Table 1:

$$IEC = \text{wt. Cl}^- / (\text{wt. polymer}) \times 1000 \text{ mmol Cl}^- / (\text{molar wt. Cl}^-)$$

The IEC of the membranes provided the concentration of chloride ions in the samples. The IEC of the membrane samples decreased with increasing time of melt pressing (Table 2). When a solvent cast membrane was melt-pressed for only 5 min, the membrane IEC was 2.2 ± 0.2 mmol.g⁻¹ but the IEC reduced to 1.6 ± 0.1 mmol.g⁻¹ when the membrane was melt pressed for 20 min. Compared to either only solvent cast or melt pressed membranes, the SCMP membranes (SCMP5, SCMP10, and SCMP20) had smaller IECs (Table 2). The IEC of 4.0 mmol.g⁻¹ for the precursor powder copolymer samples calculated from the composition of chlorine in analytical analysis reduces to 2.4 for the SCMP20 sample, with the reduction of chlorine by 40% during melt pressing. However, the chlorine reduced by only 35% when melt pressing was performed on powder copolymers for same duration of 20 min. An efficient thermally equilibrium for the thinner membrane (20 ± 3 vs 78 ± 3 μm) should contribute to the difference in chlorine reduction at the same temperature and pressure maintained for the same duration of 20 min.

For the SCMP5 sample, the IEC values measured from titrations and calculated from the elemental analysis of chlorine were similar. However, the IEC values obtained from the elemental analysis for the SCMP10 and SCMP20 membranes were higher than the values obtained from the titration. The IEC values obtained from titration systematically decreased with the melt pressing time; while the IEC from the elemental analysis stayed almost the same. The titration process involves the leaching out of chloride ions to solution before the chloride ions can be titrated whereas; the elemental analysis process involves burning the whole samples and then analysis of all chloride ions. An incomplete ion exchange process leads to a lower IEC from titration. At the same time, all chloride both counter-anion and chloride from incomplete quaternization are detected at the elemental analysis. These differences on the analysis process are partly responsible for the variations of IEC values from two different methods of calculations. The variation in IECs was more prominent for SCMP10 and SCMP20 samples probably due to the longer melt pressing time. Another possible reason to have the lower titrated IEC values is that the Cl^- ions are entrapped or buried in the bulk polymer when melt pressed for 10 min or longer to be detected during titrations, or that Cl_2 is generated and reacts with the polymer in the longer melt-pressed conditions and is not quaternized with TMA.

3.3 Ionic conductivity, water uptake, and transport properties

The time required by the AEMs to reach steady state of mass change with vapor sorption from 0 to 95 %RH was studied at 60 °C. The water uptake by the membrane reached a steady state at 60, 20, 20, 40, 40, and 60 min at 0, 20, 40, 60, 80, and 95 %RH; respectively (Figure 2a). The study was performed for two cycles of %RH steps and no hysteresis were observed for these AEMs indicating that the water uptake is fully reversible. AEMs equilibrated at 95 %RH and 60 °C overnight did not show any mass change behavior after reaching the steady state at 60 min

(Figure 2b). To provide ample time for vapor sorption study, each RH step was provided at least 60 min of humidity and temperature equilibrium time. Water uptake shown in (Figure 3) indicated a little water uptake difference below 40 %RH, but the water uptake was significantly different for the membranes above 80 %RH. At 95 %RH, the SCMP20 had a smaller λ , 14% lower, than SCMP10 and SCMP5. All membranes showed λ *ca.* 4 even at 40%RH giving the minimum number of water molecules required for ion transport [7, 37].

Liquid water uptake measurements performed on the chlorine form of the membrane showed a significant difference compared to water uptake behavior at vapor saturation. The difference in the amount of water absorption at fully saturated liquid and vapor environments is widely reported in Nafion[®] and AEMs [38-42]. The literature reports the existence of different levels of water uptake between when a membrane is equilibrated by vapor saturation or from liquid water. Li *et al.* found a difference in water uptake when membranes were equilibrated at 100 %RH compared to liquid water soaked membranes [7, 39]. The differences in water uptake can lead to the membranes having different properties, ionic conductivities, and mechanical attributes [43]. The SCMP5 membrane at 95 %RH had a water uptake of 50 wt.% compared to when the same membrane was soaked in liquid water had a water uptake of *ca.* 230 wt.%. A very similar difference in water uptake between water vapor and liquid water was observed in the ETFE-*g*-PVBtMA and PPO-*b*-PVBtMA membranes. The PPO-*b*-PVBtMA water uptake from water liquid was almost 100% higher than from water vapor [7, 8]. Membrane water-uptake was reduced with increasing time of melt pressing (Figure 3). The larger water uptake correlated positively with the increase in measured IEC.

Water swelling measured on these membranes at ambient conditions showed a greater dimensional change towards membrane thickness (through-plane) compared to any other

dimensions of the membranes (Figure 4). A relatively higher through-plane swelling is taken as a positive result since thickness swelling would increase the membrane surface contact with ionomer solutions and electrodes in electrochemical applications. Thickness changes followed the order of SCMP5 > SCMP10 > SCMP20 when measured from completely dry to completely liquid water soaked at ambient conditions. The ratio of change in thickness to width or length increases also with melt pressing time and so the degree of crosslinking, in the order SCMP5 < SCMP10 < SCMP20 where the ratio is 248, 254, 358% for thickness vs width and 299, 323, and 390% for thickness vs length. Clearly, z - swelling is a function of crosslinking but the exact mechanism is still unknown. The smaller thickness change for the SCMP20 membrane is consistent with the higher degree of crosslinking that resulted from the longer melt pressing time. All membranes showed a modest dimensional swelling in length and width directions.

Electrochemical impedance spectra in the chloride form for the membranes were measured at 95 %RH as a function of temperature. At 95 %RH and 90 °C, the Cl⁻ conductivity for the SCMP5 membrane was $115 \pm 12 \text{ mS.cm}^{-1}$. All solvent cast and melt pressed samples were more conductive than just melt pressed AEMs (Figure 5). These SCMP membranes showed linear trends for chloride and bicarbonate conductivity at 95 %RH, implying the ions were fully dissociated, in contrast to the observation for the same anions with the MP polymer that showed curved behavior, as these anions in that materials were not fully dissociated and showed VTF behavior [8]. Presumably improved morphologies of the SCMP membranes led to the observed higher ionic conductivity in all anionic forms (Figure 5) The conductivity values for the membranes were higher than the reported values of conductivity for these anions under similar operating conditions to other AEMs [12, 16, 44-46].

Because of the relative ease in measuring OH^- conductivity of AEMs in liquid water, most reports include this measurement rather than the more relevant data for OH^- conductivity as a function of RH. So to compare our SCMP AEMs with other AEMs we measured the OH^- conductivity of the SCMP10 in liquid water at 20 °C, Table 2, to be 75 mS cm^{-1} . The OH^- conductivity of the SCMP10 is three times higher than for a melt pressed sample of the polymer with a similar IEC and was comparable to the conductivity of proton observed for Nafion[®], Table 2, at 20 °C in liquid water, and is higher than for the commercial membranes A201 and FAA, although the later has a much lower IEC. In comparison to other state of the art experimental films the SCMP10 has a similar OH^- conductivity to electrospun 35%PPSU-PVBTMA, but is superior to ETFE-g-PVBTMA, although the latter has a lower IEC. A very similar trend of higher conductivity was also observed for the HCO_3^- conductivity under similar conditions of temperature and humidity. At 90 °C and 95 %RH the SCMP5 and SCMP10 HCO_3^- form of the membranes have ionic conductivities *ca.* 100 mS cm^{-1} . In general, the membranes melt pressed for shorter times than 20 minutes had higher water uptake and higher ionic conductivities.

The Arrhenius equation was used to calculate activation energies (E_a) for all the membranes. The E_a for the Cl^- and HCO_3^- conductivity for SCMP5, SCMP10, and SCMP20 membranes were very comparable, Table 3, at *ca.* 18 kJ mol^{-1} . These E_a values are similar to what are reported for Cl^- and HCO_3^- conductivities for the melt pressed membrane and a radiation grafted ETFE polymer under similar experimental conditions [7, 8].

The area specific resistance (ASR) of an AEM is the resistance of the AEM normalized by the active area of the membrane as:

$$\text{ASR } (\Omega.\text{cm}^2) = \text{resistance } (\Omega) \times \text{area } (\text{cm}^2) = \text{thickness } (\text{cm}) / \text{conductivity } (\text{S}.\text{cm}^{-1})$$

Ultimately in the design of an electrochemical energy conversion device the ASR gives an indication of the expected ohmic losses in the device and should therefore be minimized. The SCMP5, SCMP10, and SCMP20 have ASRs of 0.05, 0.04, and 0.04 $\Omega.\text{cm}^2$ for Cl^- conduction respectively at 60 °C and 95 %RH (Table 1) These membranes with, thickness of 20-30 μm , indicates that the SCMP PPO-*b*-PVBTMA could be a potential candidate for many applications.

To gain further insight into the high ionic conductivities observed in the SCMP membranes we measured the self-diffusion coefficients of water under a fully saturated environment as a function of temperature. The data could not be fit to a single component and so it was fit to two-components indicating that there were two water self-diffusion coefficients, one slower, H_2O (nmr-l), assigned to water molecules associated more strongly with the cation/anion pair and another faster, H_2O (nmr-h), assigned to water molecules more loosely bound that had self diffusion coefficients slightly less than that of bulk water. This data is shown for SCMP-5 in Figure 6a as a function of temperature and for all three films in Figure 6b at 25°C. Thus, a heterogeneous water distribution in the membrane was observed, similar to previous observations in similar AEMs [7]. The higher diffusion coefficient values gave a higher $E_a = 16-17 \text{ kJ mol}^{-1}$, the lower, more tightly bound water component had an $E_a = 9-11 \text{ kJ mol}^{-1}$, Table 3, Figure 6. Interestingly the anions studied also had E_a closer to the higher value implying that they may be solvated by the water with the higher self-diffusion coefficients, indicating that not only are the anions fully dissociated but that they move into the more loosely bound faster moving water domains. The relatively constant self-diffusion coefficients for all membranes independent of varying diffusion time (Δ) indicated no tortuosity in the water pathways on the NMR time-scale in the films, in contrast to the MP only films that had a tortuosity of 1.3 [8]. The

diffusion coefficients increased slightly for membranes melt pressed for longer. The unrestricted water diffusion on SCMP membranes would indicate that we have achieved an improvement of membrane morphology from simply melt-pressing with this processing method and hence, better transport properties of the anions are observed.

3.4 Alkaline stability

To understand the effect of processing on the membrane stability we subjected the SCMP5 and the SCMP10 membranes to a hydroxide stability test similar to a method used by Li *et al.* [47]. The bicarbonate conductivity of the membrane at various times until the end of the test after 12 days at 95 %RH and 80 °C is presented in Figure 7. Interestingly, the conductivity of the SCMP5 decreased by just 3% while the conductivity of the SCMP10 decreased by 21% over the 12-day period. Clearly, the effects of melt pressing time so the degrees of crosslinking also affect the stability of the membrane in OH⁻. The less cross-linked SCMP5 membrane was much stable than the more cross-linked SCMP10 membrane. There was no obvious change in the IR spectrum of the films as a function of exposure time to hydroxide, Figure S3.

3.5 Morphological characterization

The copolymer membrane morphology and swelling were studied using SAXS under wet and dry conditions at 60 °C, Figure 8a and b, as no differences were seen in the data as a function of temperature. A broad shoulder for the AEMs was observed that had a dependency on humidification. Relatively small changes in the SAXS due to swelling of the membranes was expected based on the lower water uptake and reduced dimensional swelling from the DVS and water uptake study above. A detail shoulder position analysis at dry and wet conditions of the membranes indicated the size of the dry d-spacing decreased to a smaller values when the membranes were wet and the difference decreased as a function of melt pressing time,

presumably as the cross-linking restrained the morphology on the nanometer scale (Table S2). For instance, the SCMP20 membrane d-spacing decreased only by 2% at wet conditions while the d-spacing for the SCMP5 decreased by 44% after swelling by water. The SCMP5 membrane had the greatest effect as it had higher water uptake, due to less cross-linking. The Porod's slope for this AEM indicated changed from -3.5 to -4.0 indicating that the clusters became more spherical as water was taken up by the film. The SCMP10 membrane showed a slightly lower slope and less spherical structures (slope less than 4.0). The SCMP20 membrane showed the least impact of swelling in the structure observed by SAXS as the size of the d-spacing did not change significantly.

3.6 Mechanical stability

The Young's modulus represents the stiffness of the membranes, the stress at break indicates the membrane's strength, and the percent elongation gives the increase in the film length from its initial length. These three parameters were used to quantify the mechanical properties of membranes.

The amount of water in the membrane affects the mechanical strength of the membranes [44]. At dry conditions, the membrane stiffness increased with the melt pressing time, and for all membranes the Young's modulus was > 400 MPa (Figure 9). The membranes were stiffer than Nafion[®] 115 [32] and other AEMs [15] measured under the similar experimental conditions. The membrane stiffness was reduced drastically, almost by ~ 80% from initial values at dry conditions when humidity of the samples was increased to 95 %RH. Vandiver *et al* have described this effect as the plasticizing effect due to water softening the membranes [44]. Similar behavior has been observed in other AEMs under similar experimental conditions [32, 43].

The stress at break of the membranes increased with increasing the melt pressing time from 5 to 20 min. The stress at break values of 16 ± 1 , 30 ± 3 , and 32 ± 6 MPa and strength of the SMP5, SCMP10, and SCMP20 membranes reduced by 51, 77, and 79%, respectively from initial dry stress at break values when humidity was increased to 95%RH at 60 °C. Much higher strength was observed for other AEMs [15] with lower IECs. Yang *et al* observed a very similar stiffness and strengths for the imidazolium form of PPO AEMs with almost one half the IECs [48]. Generally, the membrane strength reduces with the increases in ICS of the AEMs.

At dry conditions and 60 °C, membranes had the elongation of only 5-8%. However, at 95 %RH, the membrane elongation changed to 13-19%. Membrane elongation for membranes decreased in the order ~200, 150, and 75% for SCMP5, SCMP10, and SCMP20, respectively, from initial values, as the amount of cross-linking increased. Compared to other AEMs, these values are significantly lower both at dry and wet conditions. A lower elongation is better for fuel cell applications, but too little elongation might lead to mechanical cracks during the lifetimes of a device.

The high elastic modulus, moderate strength, and small elongation at dry conditions at 60 °C were reasonable; however, the large decrease in membrane stiffness and strength at wet conditions is a concern for the membranes to be used in fuel cell operating conditions of dry and wet conditions.

4 Conclusions

Uniformly thin (20 - 30 μm) membranes were prepared by solvent casting followed by melt pressing. We show that melt-pressing promotes cross-linking that generally imparts improved properties on the films. In general the SCMP AEMs had considerably improved properties over the solvent cast or melt pressed only films, with SCMP10 having the highest

anionic conductivity. The membranes melt pressed for shorter time had the higher water uptake and the higher ionic conductivity. The SCMP5 AEM was the most stable membrane to an alkaline environment at 80 °C with just 3% decrease in ionic conductivity over 12 days. The stiffness of the SCMP membranes increased with the increase in melt pressing time. The elastic modulus of membranes increased from 432 ± 14 to 724 ± 140 MPa for dry and 16 ± 1 to 32 ± 6 MPa for wet membranes when melt pressed time was increased to 20 from 5 min. Similarly, the membrane strength increased with increasing melt pressing time from 5 to 20 min for dry samples. The higher measured Cl^- in-plane conductivity for membranes melt pressed for 5 min compared to 20 min agreed with the reduction in concentration of Cl^- during melt pressing. The Cl^- and HCO_3^- conductivity values of $>100 \text{ mS.cm}^{-1}$ at 90 °C and 95 %RH were observed for membranes melt pressed for 5 min. The OH^- conductivity for the SCMP10 membranes was higher than most AEMs and was comparable to the conductivity of protons in Nafion[®] under similar experimental conditions.

The dynamic vapor sorption experiments indicated the presence of enough water molecules (λ of ~ 4) for ion transport even at 40 %RH. The Self-diffusion coefficients of water in these membranes indicates the presence of unrestricted diffusion of water, which provides the calculated pore structure tortuosity of ~ 1 . Two different values of diffusion coefficient as seen in the NMR diffusion measurement indicated an heterogeneous water distribution, namely, water associated with the cations and free water that may solvate the anions. The difference in the activation energies for each component indicated the different temperature dependency between two types of water. SAXS measurements indicated more swelling for the membranes melt pressed for the shortest duration, and almost no swelling in the microstructure for the materials SCMP for 20 minutes. A higher water uptake provided a spherical like ionic

clusters that may be related to the higher ionic transport and faster conductivity for membranes melt pressed for only 5 min.

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References

- [1] J.R. Varcoe, P. Atanassov, D.R. Dekel, A.M. Herring, M.A. Hickner, P.A. Kohl, A.R. Kucernak, W.E. Mustain, K. Nijmeijer, K. Scott, T.W. Xu, L. Zhuang, Anion-exchange membranes in electrochemical energy systems, *Energy Environ. Sci.*, 7 (2014) 3135-3191.
- [2] K.A. Mauritz, R.B. Moore, State of understanding of nafion, *Chem. Rev.*, 104 (2004) 4535-4585.
- [3] M. Piana, M. Boccia, A. Filpi, E. Flammia, H.A. Miller, M. Orsini, F. Salusti, S. Santuccioli, F. Ciardelli, A. Pucci, H₂/air alkaline membrane fuel cell performance and durability, using novel ionomer and non-platinum group metal cathode catalyst, *J. Power Sources*, 195 (2010) 5875-5881.
- [4] I. Kruusenberg, L. Matisen, Q. Shah, A.M. Kannan, K. Tammeveski, Non-platinum cathode catalysts for alkaline membrane fuel cells, *Int. J. Hydrogen Energy*, 37 (2012) 4406-4412.
- [5] M. Mamlouk, X. Wang, K. Scott, J.A. Horsfall, C. Williams, Characterization and application of anion exchange polymer membranes with non-platinum group metals for fuel cells, *Proc. Inst. Mech. Eng. A J. Power Energy*, 225 (2011) 152-160.
- [6] R. Janarthanan, A. Serov, S.K. Pilli, D.A. Gamarra, P. Atanassov, M.R. Hibbs, A.M. Herring, Direct Methanol Anion Exchange Membrane Fuel Cell with a Non-Platinum Group Metal Cathode based on Iron-Aminoantipyrine Catalyst, *Electrochim. Acta*, 175 (2015) 202-208.
- [7] T.P. Pandey, A.M. Maes, H.N. Sarode, B.D. Peters, S. Lavina, K. Vezzù, Y. Yang, S.D. Poynton, J.R. Varcoe, S. Seifert, M.W. Liberatore, V. Di Noto, A.M. Herring, Interplay between water uptake, ion interactions, and conductivity in an e-beam grafted poly(ethylene-co-tetrafluoroethylene) anion exchange membrane, *Phys. Chem. Chem. Phys.*, 17 (2015) 4367-4378.
- [8] T.P. Pandey, H.N. Sarode, Y. Yang, Y. Yang, K. Vezzù, V.D. Noto, S. Seifert, D.M. Knauss, M.W. Liberatore, A.M. Herring, A Highly Hydroxide Conductive, Chemically Stable Anion Exchange Membrane, Poly(2,6 dimethyl 1,4 phenylene oxide)-b-Poly(vinyl benzyl trimethyl ammonium), for Electrochemical Applications, *J. Electrochem. Soc.*, 163 (2016) H513-H520.
- [9] J. Ran, L. Wu, B. Wei, Y.Y. Chen, T.W. Xu, Simultaneous Enhancements of Conductivity and Stability for Anion Exchange Membranes (AEMs) through Precise Structure Design, *Sci. Rep.*, 4 (2014) 1-5.

- [10] M.A. Vandiver, B.R. Caire, S.P. Ertem, T.H. Tsai, E.B. Coughlin, A.M. Herring, M.W. Liberatore, Mechanical Performance of Polyisoprene Copolymer Anion Exchange Membranes by Varying Crosslinking Methods, *J. Electrochem. Soc.*, 162 (2015) H206-H212.
- [11] S.P. Ertem, T.-H. Tsai, M.M. Donahue, W. Zhang, H. Sarode, Y. Liu, S. Seifert, A.M. Herring, E.B. Coughlin, Photo-Cross-Linked Anion Exchange Membranes with Improved Water Management and Conductivity, *Macromolecules*, 49 (2016) 153-161.
- [12] Y. Yang, D.M. Knauss, Poly(2,6-dimethyl-1,4-phenylene oxide)-b-poly(vinylbenzyltrimethylammonium) Diblock Copolymers for Highly Conductive Anion Exchange Membranes, *Macromolecules*, 48 (2015) 4471-4480.
- [13] N. Li, L. Wang, M. Hickner, Cross-linked comb-shaped anion exchange membranes with high base stability, *Chem. Commun.*, 50 (2014) 4092-4095.
- [14] N.J. Robertson, H.A.t. Kostalik, T.J. Clark, P.F. Mutolo, H.D. Abruna, G.W. Coates, Tunable high performance cross-linked alkaline anion exchange membranes for fuel cell applications, *J. Am. Chem. Soc.*, 132 (2010) 3400-3404.
- [15] M.A. Vandiver, B.R. Caire, J.R. Carver, K. Waldrop, M.R. Hibbs, J.R. Varcoe, A.M. Herring, M.W. Liberatore, Mechanical Characterization of Anion Exchange Membranes by Extensional Rheology under Controlled Hydration, *J. Electrochem. Soc.*, 161 (2014) H677-H683.
- [16] G. Merle, M. Wessling, K. Nijmeijer, Anion exchange membranes for alkaline fuel cells: A review, *J. Membr. Sci.*, 377 (2011) 1-35.
- [17] S. Gu, J. Wang, R.B. Kaspar, Q. Fang, B. Zhang, E.B. Coughlin, Y. Yan, Permethyl Cobaltocenium ($\text{Cp}^+ 2\text{Co}^+$) as an Ultra-Stable Cation for Polymer Hydroxide-Exchange Membranes, *Sci. Rep.*, 5 (2015) 1-11.
- [18] S. Gu, Y.S. Yan, Quaternary phosphonium-based polymer electrolytes for high-performance hydroxide exchange membrane fuel cells, *Abstr. Pap. Am. Chem. Soc.*, 244 (2012) 2858.
- [19] B.Z. Zhang, S. Gu, J.H. Wang, Y. Liu, A.M. Herring, Y.S. Yan, Tertiary sulfonium as a cationic functional group for hydroxide exchange membranes, *RSC ADV*, 2 (2012) 12683-12685.
- [20] A.M. Maes, T.P. Pandey, M.A. Vandiver, L.K. Lundquist, Y. Yang, J.L. Horan, A. Krosovsky, M.W. Liberatore, S. Seifert, A.M. Herring, Preparation and characterization of an alkaline anion exchange membrane from chlorinated poly(propylene) aminated with branched poly(ethyleneimine), *Electrochim. Acta*, 110 (2013) 260-266.

- [21] M.G. Marino, K.D. Kreuer, Alkaline Stability of Quaternary Ammonium Cations for Alkaline Fuel Cell Membranes and Ionic Liquids, *ChemSusChem*, 8 (2015) 513-523.
- [22] M.R. Sturgeon, C.S. Macomber, C. Engtrakul, H. Long, B.S. Pivovar, Hydroxide based Benzyltrimethylammonium Degradation: Quantification of Rates and Degradation Technique Development, *J. Electrochem. Soc.*, 162 (2015) F366-F372.
- [23] C.R. Yang, S.L. Wang, W.J. Ma, L.H. Jiang, G.Q. Sun, Comparison of alkaline stability of quaternary ammonium- and 1,2-methylimidazolium-based alkaline anion exchange membranes, *J. Membr. Sci.*, 487 (2015) 12-18.
- [24] Q. Li, L. Liu, Q.Q. Miao, B.K. Jin, R.K. Bai, Hydroxide-conducting polymer electrolyte membranes from aromatic ABA triblock copolymers, *Polym. Chem*, 5 (2014) 2208-2213.
- [25] O.I. Deavin, S. Murphy, A.L. Ong, S.D. Poynton, R. Zeng, H. Herman, J.R. Varcoe, Anion-exchange membranes for alkaline polymer electrolyte fuel cells: comparison of pendent benzyltrimethylammonium- and benzylmethylimidazolium-head-groups, *Energ Environ Sci*, 5 (2012) 8584-8597.
- [26] S. Chempath, B.R. Einsla, L.R. Pratt, C.S. Macomber, J.M. Boncella, J.A. Rau, B.S. Pivovar, Mechanism of Tetraalkylammonium Headgroup Degradation in Alkaline Fuel Cell Membranes, *J. Phys. Chem. C*, 112 (2008) 3179-3182.
- [27] M.R. Hibbs, Alkaline Stability of Poly(phenylene)-Based Anion Exchange Membranes with Various Cations, *Journal of Polymer Science Part B-Polymer Physics*, 51 (2013) 1736-1742.
- [28] C.G. Arges, L.H. Wang, M.S. Jung, V. Ramani, Mechanically Stable Poly(arylene ether) Anion Exchange Membranes Prepared from Commercially Available Polymers for Alkaline Electrochemical Devices, *J. Electrochem. Soc.*, 162 (2015) F686-F693.
- [29] T.W. Xu, D. Wu, L. Wu, Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO)-A versatile starting polymer for proton conductive membranes (PCMs), *Prog. Polym. Sci.*, 33 (2008) 894-915.
- [30] J. Fang, Y.X. Yang, X.H. Lu, M.L. Ye, W. Li, Y.M. Zhang, Cross-linked, ETFE-derived and radiation grafted membranes for anion exchange membrane fuel cell applications, *Int. J. Hydrogen Energy*, 37 (2012) 594-602.
- [31] T.H. Tsai, S.P. Ertem, A.M. Maes, S. Seifert, A.M. Herring, E.B. Coughlin, Thermally Cross-Linked Anion Exchange Membranes from Solvent Processable Isoprene Containing Ionomers, *Macromolecules*, 48 (2015) 655-662.

- [32] B.R. Caire, M.A. Vandiver, M.W. Liberatore, Mechanical testing of small, thin samples in a humidity-controlled oven, *Rheol. Acta*, 54 (2015) 253-261.
- [33] Y.L. Tang, A.M. Karlsson, M.H. Santare, M. Gilbert, S. Cleghorn, W.B. Johnson, An experimental investigation of humidity and temperature effects on the mechanical properties of perfluorosulfonic acid membrane, *Mat Sci Eng a-Struct*, 425 (2006) 297-304.
- [34] Y. Liu, J.L. Horan, G.J. Schlichting, B.R. Caire, M.W. Liberatore, S.J. Hamrock, G.M. Haugen, M.A. Yandrasits, S. Seifert, A.M. Herring, A Small-Angle X-ray Scattering Study of the Development of Morphology in Films Formed from the 3M Perfluorinated Sulfonic Acid Ionomer, *Macromolecules*, 45 (2012) 7495-7503.
- [35] A.P. Marks, Inhibitors for vinylbenzyl chloride and vinyltoluene decomposition, in: R.A.H. Company (Ed.), U.S. Patents No. US 4087335, 1978.
- [36] R.B. Isaacson, J.P. Kennedy, Crystalline polybenzyls and process of producing same, in: E.R.E. Company (Ed.), U.S. Patents No. US3418259, 1968.
- [37] M.E. Tuckerman, D. Marx, M. Parrinello, The nature and transport mechanism of hydrated hydroxide ions in aqueous solution, *Nature*, 417 (2002) 925-929.
- [38] Q.J. Duan, S.H. Ge, C.Y. Wang, Water uptake, ionic conductivity and swelling properties of anion-exchange membrane, *J. Power Sources*, 243 (2013) 773-778.
- [39] Y.S. Li, T.S. Zhao, W.W. Yang, Measurements of water uptake and transport properties in anion-exchange membranes, *Int. J. Hydrogen Energy*, 35 (2010) 5656-5665.
- [40] A. Kusoglu, S. Savagatrup, K.T. Clark, A.Z. Weber, Role of Mechanical Factors in Controlling the Structure-Function Relationship of PFSA Ionomers, *Macromolecules*, 45 (2012) 7467-7476.
- [41] J. Benziger, A. Bocarsly, M. Cheah, P. Majsztrik, B. Satterfield, Q. Zhao, Mechanical and Transport Properties of Nafion: Effects of Temperature and Water Activity, *Struct. Bond*, 141 (2011) 85-113.
- [42] A.Z. Weber, J. Newman, Transport in Polymer-Electrolyte Membranes, *J. Electrochem. Soc.*, 151 (2004) A311-A325.
- [43] M.A. Vandiver, Effect of hydration on the mechanical properties of Anion exchange membranes, Doctoral Dissertation, Colorado School of Mines, Golden, CO, 2015.

- [44] M.A. Vandiver, B.R. Caire, T.P. Pandey, Y.F. Li, S. Seifert, A. Kusoglu, D.M. Knauss, A.M. Herring, M.W. Liberatore, Effect of hydration on the mechanical properties and ion conduction in a polyethylene-b-poly(vinylbenzyl trimethylammonium) anion exchange membrane, *J. Membr. Sci.*, 497 (2016) 67-76.
- [45] M.G. Marino, J.P. Melchior, A. Wohlfarth, K.D. Kreuer, Hydroxide, halide and water transport in a model anion exchange membrane, *J. Membr. Sci.*, 464 (2014) 61-71.
- [46] A.M. Park, R.J. Wycisk, X.M. Ren, F.E. Turley, P.N. Pintauro, Crosslinked poly(phenylene oxide)-based nanofiber composite membranes for alkaline fuel cells, *J. Mater. Chem. A*, 4 (2016) 132-141.
- [47] N. Li, Y. Leng, M.A. Hickner, C.-Y. Wang, Highly Stable, Anion Conductive, Comb-Shaped Copolymers for Alkaline Fuel Cells, *J. Am. Chem. Soc.*, 135 (2013) 10124-10133.
- [48] J. Yang, C. Liu, Y. Hao, X. He, R. He, Preparation and investigation of various imidazolium-functionalized poly(2,6-dimethyl-1,4-phenylene oxide) anion exchange membranes, *Electrochim. Acta*, 207 (2016) 112-119.
- [49] J.R. Varcoe, R.C.T. Slade, E. Lam How Yee, S.D. Poynton, D.J. Driscoll, D.C. Apperley, Poly(ethylene-co-tetrafluoroethylene)-Derived Radiation-Grafted Anion-Exchange Membrane with Properties Specifically Tailored for Application in Metal-Cation-Free Alkaline Polymer Electrolyte Fuel Cells, *Chem. Mater.*, 19 (2007) 2686-2693.
- [50] S. Gu, R. Cai, T. Luo, Z. Chen, M. Sun, Y. Liu, G. He, Y. Yan, A Soluble and Highly Conductive Ionomer for High-Performance Hydroxide Exchange Membrane Fuel Cells, *Angew. Chem. Int. Ed.*, 48 (2009) 6499-6502.
- [51] X. Wang, J.P. McClure, P.S. Fedkiw, Transport properties of proton- and hydroxide-exchange membranes for fuel cells, *Electrochim. Acta*, 79 (2012) 126-132.
- [52] R.F. Silva, M. De Francesco, A. Pozio, Solution-cast Nafion® ionomer membranes: preparation and characterization, *Electrochim. Acta*, 49 (2004) 3211-3219.

Figure Captions

Figure 1 TGA curve for weight change (Blue line) as a function of temperature (Red line) and time for PPO-*b*-PVB chloride.

Figure 2 Dynamic vapor sorption for the SCMP10 membrane in chloride form measured at 60 °C. a) vapor sorption as a function of %RH, b) Long term vapor sorption measurement at 60 °C and 95%RH; Red (%RH set point), Black (actual measured %RH), blue (measured mass change)

Figure 3 a) Water uptake (wt.%) measured as a function of relative humidity using DVS (SMS-Adv) b) λ (number of waters per charge carrier) from calculations at 60 °C. Black closed circle (●SC), Blue open circle (○ SCMP5), Black open square (□ SCMP10), Red open triangle (Δ SCMP20), and Red closed triangle (▲MP20). Dotted trend lines drawn for visual guidance.

Figure 4 a) Liquid water uptake for SCMP5 (Blue bar), SCMP10 (Black bar), and SCMP20 (Red bar) measured at room temperature. b) dimensional swelling towards; thickness (Blue bar), Width (Black bar), and Length (Red bar)

Figure 5 In-plane ionic conductivity in a) chloride b) bicarbonate forms of the membrane at 95%RH as a function of temperature; Blue open circle (○ SCMP5), Black open square (□ SCMP10), Red open triangle (Δ SCMP20), and Red closed triangle (▲MP20). Dotted trend-lines drawn for visual guidance.

Figure 6 Self-diffusion coefficient of water in a) SCMP5 membrane at full saturation conditions of water measured as a function of diffusion time at 25 °C (Blue circle), 30 °C (Blue square), 40 °C (Black triangle), 50 °C (Red diamond) b) SCMP5 (Blue open circle, ○), SCMP10 (Black open square, □ SCMP10), and SCMP20 (Red open triangle, Δ SCMP20) all measured at saturation and 25 °C. Dotted trend-lines drawn for visual guidance.

Figure 7 Bicarbonate conductivity measured at 80 °C and 95%RH after the membranes were soaked in 1 M KOH solution at 80 °C, Blue open circle (○ SCMP5), Black open square (□ SCMP10). Dotted trend-lines drawn for visual guidance.

Figure 8 SAXS of AEMs SCMP5, circles, SMP10, squares, SCMP20, triangles, at a) dry and b) wet conditions at 60 °C

Figure 9 Membrane strength was tested using Young's modulus, stress at break, and elongation using ARES-G2 (TA instrument Inc.) as a function of dry (Red bar) and 95%RH (Blue bar) at 60 °C.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Tables

Table 1 The membrane thickness, titrated IEC, and ASR calculated at 60 °C and 95%RH

Membrane samples	Thickness (μm)	IEC-Titration (mmol.g ⁻¹)	IEC-Elemental Analysis (mmol.g ⁻¹)	ASR (Ω.cm ²)
Powder	-	-	4.0 ± 0.1	-
SCMP5	31 ± 3	2.2 ± 0.2	2.2 ± 0.5	0.05
SCMP10	26 ± 3	1.8 ± 0.2	2.3 ± 0.1	0.04
SCMP20	20 ± 3	1.6 ± 0.1	2.4 ± 0.1	0.04
MP	78 ± 3	2.6 ± 0.1	-	0.21

Table 2 Comparative study of OH⁻ conductivity in AEMs with similar IECs

Membrane samples	IEC	Conductivity (mS.cm ⁻¹)	Measured conditions	References
SCMP5 (Cl ⁻)	2.2 ± 0.2	67 ± 9	60 °C, 95 %RH	This work
SCMP10 (Cl ⁻)	1.8 ± 0.2	66 ± 10	60 °C, 95 %RH	This work
SCMP20 (Cl ⁻)	1.6 ± 0.1	46 ± 5	60 °C, 95 %RH	This work
SCMP10 (OH ⁻)	1.8 ± 0.2	75 ± 25	20 °C, liquid water	This work
PPO- <i>b</i> -PVBtMA (OH ⁻)	1.7	25 ± 1	20 °C, liquid water	[12]
PPO- <i>b</i> -PVBtMA (OH ⁻)	3.2	87 ± 3	20 °C, liquid water	[12]
PPO- <i>b</i> -PVBtMA (OH ⁻)	3.2	138 ± 9	60 °C, 95 %RH	[8]
PPO- <i>b</i> -PVBtMA (OH ⁻)	2.9	106 ± 13	60 °C, 95 %RH	[8]
ETFE- <i>g</i> -PVBtMA (OH ⁻)	1.8	112 ± 20	60 °C, 95 %RH	[7]
ETFE- <i>g</i> -PVBtMA (OH ⁻)	1.03	27	20 °C, liquid water	[49]
35%PPSU-PVBtMA (OH ⁻)	2.6	66	23 °C, liquid water	[46]
FumaTech® FAA (OH ⁻)	0.91	17	20 °C, liquid water	[50]
Tokuyama® A201	1.62 ± 0.01	32.8 ± 0.6	23 °C, liquid water	[51]
Nafion® 115 (H ⁺)	0.92	76 ± 8	25 °C, liquid water	[52]

Table 3 Activation energies for ions/water calculated using Arrhenius equation

Species	Activation Energy, Ea (kJ/mol)		
	SCMP5	SCMP10	SCMP20
Cl ⁻ (c)	19 ± 5	17 ± 2	15 ± 4
HCO ₃ ⁻ (c)	19 ± 5	18.8 ± 0.4	20 ± 3
H ₂ O (nmr-h)	17	17	16
H ₂ O (nmr-l)	9	11	10

(c) represents activation measured from in-plane ionic conductivity, nmr-h and nmr-l represent the activation energies calculated using the higher and the lower diffusion coefficient component values measured using the solid-state NMR